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## LETTER

# Ionic Liquid Mediated Deposition of Ruthenium Mirrors on Glass under Multiphase Conditions

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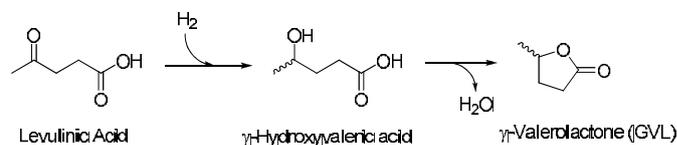
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**At 150 °C and 6 atm of H<sub>2</sub>, shiny metallic mirrors of Ru nanoparticles (2-4 nm) have been deposited on borosilicate glass by the assistance of a multiphase system comprised of methyl trioctyl ammonium bistriflimide as an ionic liquid, RuCl<sub>3</sub> as a metal precursor, and an aqueous solution of an organic (acetic or levulinic) acid or acetyl acetone as metal coordinating agents.**

The silvering process for the fabrication of mirrors has been among the first reported applications of metal films deposited on a support to obtain a glassy reflective surface.<sup>1</sup> In this respect, the use of Ru has received attention from 1956 when the reduction of RuCl<sub>3</sub> by SnCl<sub>2</sub> was patented to provide Ru mirrors on glass and other ceramic materials.<sup>2</sup> Since then, more sophisticated sputtering techniques have been described to deposit Ru-Mo alloys on sapphire slabs for mirrors of instrumental devices,<sup>3</sup> Ru films on glass for applications in the visible and IR,<sup>4</sup> multilayer mirrors of Ru/Si and Ru/Mo/Be on silicon wafers for soft-X-ray optical elements and extreme ultraviolet (EUV) lithography,<sup>5</sup> and optical mirrors for Micro Electro-Mechanical Systems (MEMS).<sup>6</sup> The literature also reports Ru coatings obtained by electrochemical deposition (electroplating) on glass substrates,<sup>7</sup> while other chemical deposition methods are indeed quite rare. To the best of our knowledge, only one paper refers to Ru-mirrors achieved through the covalent functionalization of Si substrates with a multidentate ligand {TMPEDA: N-[3-(trimethoxysilyl)propyl]ethylenediamine triacetate} followed by the

complexation of [Ru(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>.<sup>8</sup> We wish to describe herein an original procedure for the deposition of highly stable mirrors of Ru stabilized on glass mediated by chemical reactions occurring in multiphase systems comprised by ionic liquids (ILs). Such multiphase arrangements (MILs) are usually composed of three immiscible organic, aqueous and IL phases which provide unique reaction environments due to the segregation of organic reagents, products and metal catalysts in the different compartments of the system.<sup>9</sup> MILs have been extensively investigated by our group:<sup>9,10</sup> one recent application has involved the catalytic hydrogenation/dehydration of bio-based levulinic acid (LA) to  $\gamma$ -valerolactone (GVL, Scheme 1).<sup>11</sup>



**Scheme 1.** Hydrogenation/dehydration of LA to GVL

In a typical reaction, a 25-mL tubular reactor of borosilicate glass (Pyrex) was charged with equal volumes (4.4 mL) of isooctane and an aqueous solution of LA (7.87 mmol, 1.8 M), trioctyl methyl ammonium bistriflimide ([N<sub>8881</sub>][NTf<sub>2</sub>]) as an ionic liquid (0.85 g, 1.36 mmol), and RuCl<sub>3</sub> (20 mg, 0.097 mmol) as a catalytic precursor. The vessel was then placed in an autoclave at 150 °C and 35 atm of H<sub>2</sub> for 16 hours. Under such conditions, the reduction of the metal salt to Ru(0) took place followed by the stabilization of Ru-nanoparticles in the ionic liquid phase.<sup>11,12</sup> This not only improved the performance of the catalyst, but allowed its reuse up to nine recycle tests with quantitative conversion and complete selectivity to GVL. Although the reaction occurred in water (both LA and GVL are highly water soluble), the use of *i*-octane – apparently inconsequential – was functional to phase separation and recovery of product and catalyst. An unexpected behaviour was observed once the procedure was reproduced using a glass reactor previously cleaned in hot aqua

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† Electronic Supplementary Information (ESI) available: Synthesis and characterization of trioctyl methyl ammonium bistriflimide, RuCl<sub>2</sub>(acac)(acacH), and Ru(acac)<sub>3</sub>. ICP analyses and selection of TEM/SEM images. See DOI: 10.1039/x0xx00000x

regia: at complete conversion of LA to GVL, the liquid mixture was removed leaving a shiny, metallic mirror perfectly anchored to the inner walls of the reactor and indefinitely stable on the shelf (Figure 1).



**Figure 1.** Detail of a metallic mirror deposited on a glass reactor under multiphase conditions

Of note, not even traces of such a deposition were noted in the absence of the ionic liquid. Inspired by this result, we were prompted to investigate this peculiar phenomenon through the screening in search for optimal experimental (multiphase) conditions and the full characterization of the mirrors by electron microscopy techniques.

**Multiphase conditions.** Initial experiments demonstrated that the mirror formation was successful only if the glass reactor was subjected to a strong oxidising pretreatment: hot aqua regia (70 °C, 6 h) or a combined cycle using a 1:1 mixture of concd. hydrochloric acid and methanol (rt, 30 min) followed by concd. sulfuric acid (rt, 30 min) and boiling water (30 min).<sup>13</sup> Thereafter, the investigation was focused on the role of the organic acid and of the hydrocarbon (*i*-octane) and water phases in the multiphase deposition process.

The above described procedure was carried out with different organic acids including formic, acetic, pyruvic, and succinic acid that were chosen according to their similarity of structure and/or properties (pKa and water solubility,<sup>4</sup>) to LA. Two model mineral acids such as HCl and H<sub>2</sub>SO<sub>4</sub> were also considered. Moreover, multiphase experiments were compared with and without *i*-octane and water.<sup>5</sup> At the end of each test, residual liquid mixtures were removed and the reflection phenomenon, if occurring, was exclusively due to the solid deposited on the glass reactor. The recovered liquid mixtures had variable (yellow-to-brown) colors, but they did not possess any reflective feature. Results are summarized in Table 1.

The hydrocarbon phase proved inconsequential, but the presence of water (entries 1-4), and even more importantly, the nature of the acid were critical for the formation of shiny deposits. LA was efficiently replaced by acetic acid (cf. entries 2 and 4), but other compounds produced non uniform and opaque coatings (formic and pyruvic acid, entries 1 and 3), or they were not effective at all (succinic acid in entry 5, and mineral acids not shown in the Table). Further tests proved that the formation of mirrors could be achieved also under a lower H<sub>2</sub> pressure of 6 bar, and that the overall process was insensitive to the acid amount and to its subsequent reduction (cf. Scheme 1).

In particular, visual inspections of coatings showed no alteration in gloss and homogeneity even when: i) the concentration of LA (or acetic acid) was varied by a factor of 32 (from 0.22 to 7.1 M) in subsequent multiphase tests; ii) not even traces of hydrogenated derivatives of acetic acid (acetaldehyde or ethanol) were detected in the final reaction mixture.<sup>3</sup> This clearly demonstrated that the organic acid was not functional to the pH control of the aqueous solution.

**Table 1.** Effect of organic acids on glass deposition under multiphase conditions<sup>a</sup>

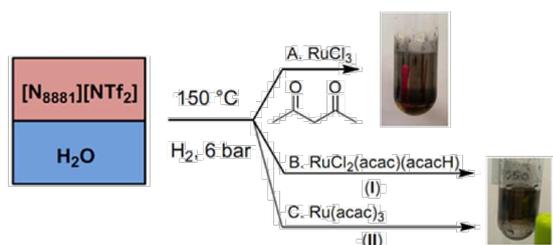
Entry	Acid, pKa	Water	Deposition on glass <sup>b</sup>
1	HC(O)OH, 3.77 (formic)	Yes	
		No	None
2	MeC(O)OH, 4.76 (acetic)	Yes	
		No	None
3	MeCOC(O)OH, 2.50 (pyruvic)	Yes	
4	MeCO(CH <sub>2</sub> ) <sub>2</sub> C(O)OH, 4.61 (levulinic)	Yes	
		No	None
5	HO(O)C(CH <sub>2</sub> ) <sub>4</sub> C(O)OH, 4.43 (succinic)	Yes	None

<sup>a</sup> Multiphase system: aqueous solution of acid (7.87 mmol, 1.8 M; 4.4 mL), [N<sub>8881</sub>][NTf<sub>2</sub>] (0.85 g, 1.36 mmol), and RuCl<sub>3</sub> (20 mg, 0.097 mmol). 150 °C and 35 atm of H<sub>2</sub>. All experiments were carried out in the presence and absence of isooctane (4.4 mL).<sup>b</sup> Pictures of the coating of glass reactors. Entries 1 and 3: non reflective deposits with formic and pyruvic acid. Entries 2 and 5: mirror-looking films with acetic and levulinic acids. Fuchsia lines show the reflection of a coloured object on the deposits.

A literature survey prompted us to consider a different option: in particular, since procedures for the synthesis of Ru(III) β-diketonate complexes described occasional side-reduction reactions with formation of metal deposits,<sup>14</sup> three additional multiphase experiments (A-C) were devised in the presence of acetylacetonate as a model chelating β-diketone,<sup>15</sup> and two Ru(III)-complexes such as dichloro acetylacetonato acetylacetonate ruthenium (III) [RuCl<sub>2</sub>(acac)(acacH), **I**] and tris-acetylacetonate ruthenium (III) [Ru(acac)<sub>3</sub>, **II**]. Reactions A-C were carried out at 150 °C and 6 bar, without isooctane, by adjusting the conditions of entry 2 in Table 1. In the first test (A), acetic acid was replaced by an equimolar amount of acetylacetonate (7.87 mmol). In the second and third tests, acetic acid was removed and RuCl<sub>3</sub> was replaced by compound **I** and **II** for test B and C, respectively.<sup>16</sup> Both complexes were used in the same molar amount as RuCl<sub>3</sub> (Scheme 2).

Test A afforded a shiny mirror comparable to those described in Table 1 (top) and reflective deposits were achieved also in the presence of compounds **I** and **II**, albeit less consistent (tests B and C, bottom). These results were consistent with a deposition phenomenon triggered by the coordination of Ru(III) to ligands of suitable geometry and binding power. Accordingly, the formation of mirrors described in Table 1 plausibly started with the chelation of RuCl<sub>3</sub> by levulinic or acetic acid to produce the corresponding carboxylate complexes.<sup>17</sup>

Moreover, the occurrence of Ru(III)-β-diketonate or -carboxylate species in water could also decrease the reduction potential of the metal,<sup>18</sup> thereby favouring the overall process of deposition of Ru(0).



**Scheme 2.** Multiphase depositions with  $\text{RuCl}_3$ /acetylacetone (A) and complexes I and II (B and C)

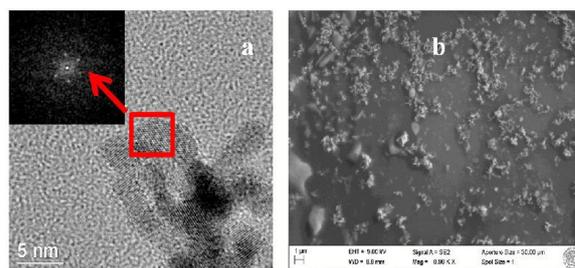
This aspect along with the solubility of Ru-complexes (both diketonates and carboxylates,<sup>17,18</sup>) in water offered an explanation for the role of the aqueous medium in the investigated multiphase system. It should be noted that also the metal coordinating capability of the tested organic acids was plausibly favoured by their solubility in aqueous solutions. Among acids of Table 1, succinic acid was the only sparingly water-soluble compound (see note †): at the same time, it proved completely ineffective for the deposition of metallic Ru (entry 5).

**Characterization of mirrors.** High Resolution Transmission Electron Microscopy (HRTEM) and Scanning Electron Microscopy (SEM) coupled with Energy- X-ray Analysis (EDX) were used to characterize the structure and morphology of the mirrors. The aim was to understand the form (amorphous or crystalline) of Ru deposits as well as the role of  $([\text{N}_{8881}][\text{NTf}_2])$ . Specimens for TEM were prepared by gently scraping the mirror from the glass support and then suspending the powder in isopropanol. A drop of such a suspension was deposited on a holey carbon coated Cu grid which, after solvent evaporation, was inserted into the TEM. SEM experiments were done on small pieces (2x2 mm) of mirrored glass. Figures 2a and 2b report HRTEM and SEM (in plan view) images, respectively, of the model mirror obtained with AcOH (entry 2 of Table 1). HRTEM analysis revealed that the Ru was in the form of crystalline nanoparticles of ~3 nm (Figure 2a), while SEM pictures showed an ensemble composed of many agglomerates characterized by a rough surface surrounded and, in some cases, almost completely covered by a smooth solid surface (Figure 2b). The chemical composition of this system was then determined by EDX which proved that aggregates were Ru particles, while the surface was constituted by the IL.

Similar results were observed by TEM, SEM, and EDX analysis of other mirrors obtained with different amounts of AcOH, and with levulinic acid or acetylacetone (entry 4 of Table 1 and Scheme 2, respectively). Deposits were always formed by crystalline Ru nanoparticles of 2-6 nm embodied in an IL matrix. Moreover, SEM analysis in cross section of different samples confirmed that the IL effectively covered the glass surface generating a film of an extremely variable thickness from nanometres to microns.

To further characterize samples of mirrored glass, both ICP-AES analyses and tests of chemical stability were carried out. Irrespective of the complexing agent used, ICP measures proved that the deposition yield of Ru on mirrors was in the range of 70-80%.<sup>#</sup> ICP also demonstrated that mirrors were stable since no Ru leaching

occurred when deposits were subjected to a range of acid and basic conditions.



**Figure 2.** Left, figure 2a, HRTEM of Ru nanoparticles, the inset is the Hanning masked FFT of the nanoparticle enclosed in the red square and oriented along the [001] ZA, showing the {100} and {1-10} reflections of the hexagonal Ru. Right, figure 2b, SEM in plan view showing Ru agglomerates and the IL.

However, a fast and complete removal of the metal was observed by treatment with aq. NaClO (even common bleach was effective) producing ruthenium tetroxide.<sup>19</sup> Once the metal was released, the organic matrix composing the original mirror was recovered and analysed by NMR. This confirmed that the structure of the ionic liquid  $([\text{N}_{8881}][\text{NTf}_2])$  was fully preserved.

Results of deposition and characterization tests are consistent with a multistep formation of Ru mirrors. At first, the initial acid cleaning of glass not only removes impurities, but it induces an oxidative stress which favours the formation of surface silanol groups.<sup>20</sup>

Such groups activate the reactor walls towards the adsorption of  $[\text{N}_{8881}][\text{NTf}_2]$  via non covalent (acid-base and H-bonding) interactions similar to those reported between ionic liquids and different supports, including silica, activated carbon and carbon nanotubes.<sup>21</sup> This allows the growth of an organic-IL layer onto the glass surface. Then,  $\text{RuCl}_3$  (plausibly partitioned in the aqueous and IL phases) is converted into a  $\text{Ru(III)}-\beta$ -diketonate or -carboxylate complex whose formation facilitates the reduction of the metal. Finally, once  $\text{Ru(0)}$  is formed, it is dispersed in the form of crystalline nanoparticles in the IL phase. Although the (electrosteric) stabilising effect of metal NPs in ILs is widely documented in the literature,<sup>22</sup> the present case describes a peculiar unprecedented situation whereby the IL  $([\text{N}_{8881}][\text{NTf}_2])$  is immobilized as a film fixed to the glass. Such an organic layer may therefore reduce not only the natural roughness of the surface of metal NPs, but also their mobility by forcing them within a flat thin film coating. These aspects offer an explanation for the ability of the investigated deposits to reflect light. Of note, in the biphasic liquid-liquid hydrogenation of olefins over Rh and Ir-NPs stabilised by imidazolium salts, the passivation of glass reactors with  $\text{Me}_3\text{SiCl}$  has been reported to avoid the deactivation of nanocatalysts.<sup>23</sup>

In conclusion, this paper describes an original and simple procedure by which an IL-based multiphase system assists the deposition of highly stable Ru mirrors on borosilicate glass. The technique offers well reproducible results: electron microscopy and NMR confirms that deposits are composed of Ru nanoparticles of 2-6 nm embedded on a support of  $[\text{N}_{8881}][\text{NTf}_2]$  whose structure is not modified by the deposition process. However, the mechanism of mirror formation is far from being understood, and the overall potential of the method is largely unexplored. The use of different ionic liquids, metal salts

(even as binary/ternary mixtures) of the Pt-group and glass supports will be the object of future investigations.

## Experimental

**Materials.** RuCl<sub>3</sub>, carboxylic (formic, acetic, pyruvic, levulic, and succinic) acids, acetyl acetone, mineral acids (HCl and H<sub>2</sub>SO<sub>4</sub>), and NaClO were analytical grade reagents from Sigma Aldrich. Deionized MilliQ was used in all deposition experiments.

ICP-OES analysis were run using a Perkin Elmer Optima 5300DV. <sup>1</sup>H NMR were recorded at 300 MHz, <sup>13</sup>C spectra at 75 MHz and chemical shift were reported in δ values downfield from TMS; CDCl<sub>3</sub> was used as solvent. Transmission Electron Microscopy (TEM) images were acquired on JEOL JEM 3010 TEM operating at 300 kV, while SEM measurements were performed on a Sigma-VP Field Emission.

**Deposition of Ru Mirrors.** In a typical deposition experiment, a 25-mL tubular reactor of borosilicate glass (Pyrex) was subjected to an acid treatment by a 1:1 mixture of concd. hydrochloric acid and methanol (20 mL in total, rt, 30 min) followed by concd. sulfuric acid (20 mL rt, 30 min) and boiling water (20 mL, 30 min). Then, the reactor was charged with an aqueous solution (4.4 mL) of a carboxylic acid (levulinic or acetic, 7.87 mmol) or acetyl acetone (7.87 mmol), trioctyl methyl ammonium bistriflimide ([N<sub>8881</sub>][NTf<sub>2</sub>]) as an ionic liquid (0.85 g, 1.36 mmol), and RuCl<sub>3</sub> (20 mg, 0.097 mmol) as a catalytic precursor. The vessel was placed in a steel autoclave at 150 °C and 6 atm of H<sub>2</sub> for 16 hours. Thereafter, the residual liquid solution was removed and the deposit of metallic mirror of Ru nanoparticles on glass was thoroughly washed with water, before proceeding to characterization tests by TEM and SEM.

## Acknowledgements

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## Notes and references

‡ Except for succinic acid whose solubility in water is of 2.4 g/100 mL, all other acids are miscible in water in all proportions.

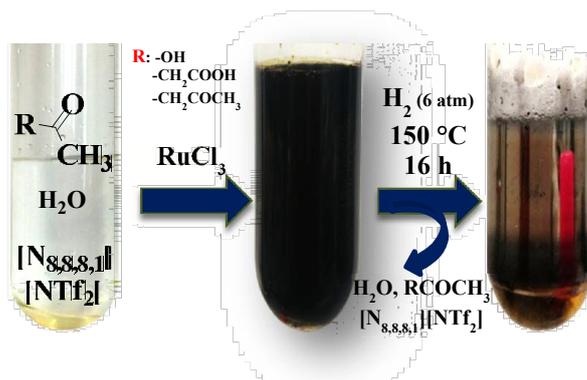
§ In the absence of *i*-octane, the starting system was an ionic liquid/water biphasic arrangement. In the absence of both water and *i*-octane, the metal salt (RuCl<sub>3</sub>) was suspended in the ionic liquid phase.

¶ However, very preliminary results suggested that such Ru deposits on glass could act as catalysts for model hydrogenation reactions: for example, in the presence of the Ru coating of entry 4 of Table 1, at 60 °C and 1 atm of H<sub>2</sub>, nitrobenzene (6·10<sup>-3</sup> M; ethanol solvent, 10 mL) was quantitatively converted to aniline in 16 hours.

# ICP analyses were carried out on a total of 6 samples, three obtained from deposition tests with AcOH (Table 1, entry 2), and other three with acetylacetone (Scheme 2, top). The Ru content (by ICP) was evaluated in the liquid mixtures recovered at the end of deposition experiments. (See ESI).

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Stable mirrors of Ru nanoparticles are deposited on borosilicate glass by an ionic liquid and a metal coordinating agent.